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IN HYDROCARBON MIXTURES

By Harold F. Hipsher

Aircraft Engine Research Laboratory
Cleveland, Ohio

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RESTRICTED BULLETIN

A METHOD FOR THE DETERMINATION OF AROMATICS IN HYDROCARBON MIXTURES

By Harold F. Hipsher

SUMMARY

A method has been developed for the estimation of aromatic hydrocarbons in hydrocarbon mixtures. Aromaticity of the mixture is estimated from the change in refractive index that results from the removal of the aromatic portion by a sulfuric acid extraction and subsequent percolation through silica gel. The method is simple and requires approximately 2.5 hours. No attempt is made to identify the individual aromatics.

The method was tested with nine base stocks containing aromatics in concentrations from 0 to 35 percent by volume. A mean deviation of ± 0.17 percent was obtained with a maximum error of -0.5 percent. The accuracy of the determination is impaired by the presence of olefins, but the resulting error is insignificant for most aviation fuels in which the olefin content is small. Aromatic amines also interfere and are removed before the determinations are made.

INTRODUCTION

An accurate and rapid method of quantitatively determining the percentage of aromatics in fuel blends is desirable for laboratory analysis of fuels. The current increased aromatic content of aviation fuels makes the analysis for aromatics particularly important.

Numerous methods of determining the aromatic content of hydrocarbon mixtures have been suggested. Extraction of aromatics from gasoline by treatment with concentrated sulfuric acid (as in spec. AN-VV-F-786) offers a means of determining aromaticity, but the results are unreliable because of incomplete sulfonation and difficult separation of the acid and the hydrocarbon phases. An approximate analysis based on the relative solubility of picric acid in paraffinic and aromatic hydrocarbons has been used at the Ethyl Laboratories. The National Bureau of Standards (reference 1) has

developed a procedure in which the volume of aromatic-free filtrate resulting from passing a fuel through a definite amount of standard adsorbent is compared with the volume obtained from known mixtures. Analysis by the NBS method as well as by methods based on properties such as specific dispersion (reference 2) or ultraviolet-light absorption (reference 3) requires fractionation of the unknown mixture into narrow boiling ranges.

A convenient and reasonably accurate method of determining the aromaticity of aviation fuels was developed by the Bureau of Aeronautics, Navy Department. This method, which requires a minimum of equipment and time, essentially consists in the determination of the percentage of aromatics from the change in the index of refraction of the hydrocarbon mixture after extraction with sulfuric acid and percolation of the hydrocarbon layer through a silica gel adsorbent. The accuracy of the method has been improved and its applicability extended at the NACA Cleveland laboratory by slight modifications in the mathematical computations. The complete procedure is described herein and its applicability is demonstrated by the determination of the aromaticity of 24 hydrocarbon mixtures prepared from four pure aromatics, three aromatic mixtures, three pure base compounds, and six aviation base fuels.

PRESENTATION OF THE METHOD

Apparatus and Materials

An Abbe refractometer having a precision of ± 0.0001 was used in the research. The temperature of the instrument was kept at $20^\circ \pm 0.1^\circ \text{C}$ by water circulated through it from a thermostatically controlled bath.

The adsorption columns were constructed of 18-millimeter glass tubing, 76 cm long, and were filled with silica gel of 28 to 200 mesh stabilized at 650°F . A 100-milliliter round-bottom flask was sealed to the top of each column to provide a reservoir for the fuel mixtures. The entire length of each of the columns was cooled with a water jacket.

The fuels used in the investigation and their refractive indices are listed in table I. (Index of refraction n_D^{20} is, for simplification, designated n throughout this report.) Aromatic components in the base stocks were removed before the known fuel mixtures were prepared. The removal was accomplished by repeated percolation through

silica gel until the absorption of each base stock in the ultra-violet light region was no more than spectrographic isooctane containing less than 0.01 percent aromatics. The absorption was measured by a Beckman quartz spectrophotometer. The aromatics were better than 99 percent pure as prepared at the Cleveland laboratory. Fuels 19, 20, and 21 were prepared to represent aromatic mixtures typical of those in current aviation fuels, such as AN-F-28.

Samples of known aromatic concentrations were prepared by measuring both the base stocks and the aromatic hydrocarbons from burettes into volumetric flasks. Glassware recalibrated with hydrocarbons was used to measure all volumes. Because the volume change on mixing was found to be less than one part in a thousand, the volume percentage of aromatics in each mixture was considered to be sufficiently precise for all practical purposes.

Procedure for Analysis

The index of refraction of the hydrocarbon mixture being analyzed is determined at $20^{\circ} \pm 0.1^{\circ}$ C. A 100-milliliter quantity of the mixture is then cooled to below 10° C and extracted with two 125-milliliter portions of sulfuric acid (66° Bé). (This step is unnecessary when the aromatic concentration of the mixture is less than 5 percent by volume.)

The hydrocarbon layer from the acid extraction is again chilled to below 10° C and placed in the adsorption-column reservoir. The sample is percolated by gravity through the silica gel and collected at the bottom of the column in 5-milliliter fractions. The receivers are cooled to avoid excessive losses of low-boiling components. The foregoing procedure removes the dyes used to designate leaded fuel, but the error introduced is negligible.

The index of refraction of each fraction of filtrate is determined. These values are plotted against volume collected to obtain an analysis curve. The analysis curves generally have a characteristic shape similar to that shown in figure 1. The first fractions have higher indices of refraction than those immediately following. This effect is probably caused by partial fractionation of the first few milliliters of the sample from heat released in wetting the silica gel. The curve gradually flattens out to a minimum value, at which point the removal of aromatics is complete, and then rises as the gel becomes saturated with aromatics. The index of refraction of the base stock is defined by the flat portion of the curve. Infrequently the analysis curve will not show a constant index of

refraction on either side of the minimum point, which is an indication that the silica gel has become saturated before the aromatics are completely removed. In such instances a new sample of the hydrocarbon mixture is extracted with sufficient sulfuric acid to assure the lowering of the aromatic content below 5 percent. In some cases a sample larger than 100 milliliters should be used in order that a sufficient volume remains after the acid extractions for percolation through the silica gel.

The experimental procedure requires approximately 2.5 hours for completion of a single determination. The average time per determination is less if several are made concurrently.

RESULTS AND DISCUSSION

Figure 2 presents typical refractive-index data for blends prepared with toluene and several base stocks. Refractive-index data plotted for nearly all of the binary blends of the aromatics and base stocks listed in table I showed trends similar to those in figure 2. Under the concentration range investigated, the relation between refractive index and percentage aromatic have been found to be linear. The extrapolated index values at 100-percent aromaticity, however, do not correspond exactly to the refractive index for the pure aromatic employed, which shows that the blending relation cannot be linear in the aromatic-rich range. These "apparent" indices of refraction at 100-percent aromaticity are designated hereinafter by n_a .

Values of the extrapolated apparent indices of refraction n_a for the various binary blends at 100-percent aromaticity are shown in table II. Average apparent indices \bar{n}_a are also shown for a single aromatic in a large number of base stocks as well as average values for several aromatics in a single base stock. The average index of refraction for the various aromatics in a single base stock are plotted in figure 3 against the refractive index of the particular base stock at 0-percent aromaticity n_b . The mean of these average values is 1.4926.

By virtue of the linear nature of the curves shown in figure 2, it is possible to superimpose all refractive index-composition data upon a single straight line by plotting the ratio $(n_x - n_b)/(n_a - n_b)$ against the corresponding percentage aromatics, where n_x is the index of refraction of the binary blend.

When unknown mixtures are analyzed, the value of n_a is generally unknown because of uncertainty in the nature of the aromatic and the base stock used. If the base stock is known and the aromatic unknown, \bar{n}_a should be used. If both base stock and aromatic are unknown, the mean of several \bar{n}_a values should be used. The magnitude of the errors introduced by the use of the mean of \bar{n}_a values rather than \bar{n}_a for a particular base stock may be seen from a comparison of the last three columns in table III. The first of these columns corresponds to the composition of the blend as prepared. The second of these columns gives analytical results obtained with these blends using \bar{n}_a values shown in the vertical column of table II and plotted in figure 3. The third column includes analytical results computed on the basis of a single average value (1.4926) intended to represent all aromatics in all base stocks.

For most base stocks the error introduced by using this single average value for \bar{n}_a is insignificant. The error introduced by using the value of 1.4926 is significant only in base stocks having a refractive index considerably outside the aviation-fuel range (less than 1.3900 or greater than 1.4100). Thus, low results are obtained for cyclohexane ($n_b = 1.4259$) and high results for neohexane ($n_b = 1.3689$). For most aviation gasolines, then, the volume percentage of aromatics in a given hydrocarbon mixture may be expressed as

$$\frac{n_x - n_b}{1.4926 - n_b} \times 100$$

The presence of olefins in large percentages causes interference in the determination of aromatic content. An olefin content of 2 percent will cause an error of approximately 0.2 to 0.5 percent in the determination. The presence of olefins and an indication of the amount may be shown by a bromine-number determination (U.O.P. Method No. H-44-40).

Aromatic amines change the refractive index of a gasoline and, as the olefins, are removed in the procedure. Therefore, the amine must be removed by extracting with approximately 18-percent hydrochloric acid before the determination of aromatics is made. Up to 6 milliliters of the amine per 100 milliliters of gasoline may be extracted with two 25-milliliter portions of 18-percent hydrochloric acid. The gasoline must be washed once with water after the extraction to remove the hydrochloric acid from the gasoline phase. The amines must be extracted before the bromine number is determined because of the reaction between bromine and the amine.

CONCLUSIONS

The change in refractive index of a hydrocarbon mixture upon removal of aromatics can be employed to determine the aromatic content of such a mixture with a maximum error of about 0.5 percent. The method is rapid and requires only a small amount of apparatus. Olefins interfere in the method; but the small amounts usually found in aviation fuels cause no significant error. Aromatic amines also interfere and must be removed before the aromaticity is determined.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio.

REFERENCES

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3. Cleaves, A. P.: Ultraviolet Spectrochemical Analysis for Aromatics in Aircraft Fuels. NACA ARR No. E5B14, 1945.

TABLE I - DESCRIPTION OF FUELS

Type of fuel	Fuel	Composition	Index of refraction, n
Base stocks	1	Baton Rouge virgin base stock, Esso Lab., sample No. 745-43	1.3936
	2	Bayonne Refinery virgin base stock, Esso Lab., sample No. 744-43	1.3965
	3	Mixed Texas and Hobbs crudes, Shell Oil Co.	1.3915
	4	91-octane straight-run base stock, Sun Oil Co.	1.4052
	5	69-octane deparaffinized straight-run base stock from selected coastal crudes, Texas Co.	1.4058
	6	Deparaffinized straight-run base stock, Texas Co. of Calif.	1.4031
	7	Neohexane (c.p.), Phillips Petroleum Co.	1.3689
	8	Cyclohexane (c.p.), Barret Division of Allied Chemical & Dye Corp.	1.4259
	9	50 percent fuel 8 plus 50 percent fuel 2	1.3846
	10	50 percent fuel 7 plus 50 percent fuel 6	1.4149
	11	S-2 reference fuel	1.3914
Aro-matics	12	Benzene	1.5001
	13	Cumene	1.4910
	14	Toluene	1.4963
	15	Ethylbenzene	1.4955
	16	p-Xylene	1.4954
	17	n-Butylbenzene	1.4892
	18	sec-Butylbenzene	1.4898
	19	5 parts xylenes, 2 parts cumene, 1 part toluene	1.4936
	20	54 percent cumene, 32 percent xylenes, 11 percent toluene, 3 percent benzene	1.4927
	21	9 percent cumene, 60 percent xylenes, 26 percent toluene, 5 percent benzene	1.4943

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TABLE II - APPARENT REFRACTIVE INDEX n_a AT 100-PERCENT AROMATICITY

Base stock \ Aromatic ↓ →	12	13	14	15	16	17	18	19	20	21	Average apparent refractive index \bar{n}_a of several aromatics in one base stock
1	1.4943	1.4920	1.4923	-----	1.4945	-----	1.4943	1.4953	1.4965	1.4953	1.4943
2	1.4953	1.4924	1.4930	-----	1.4935	-----	1.4922	1.4942	1.4937	1.4948	1.4937
3	1.4900	1.4900	1.4922	-----	1.4900	-----	1.4903	1.4909	1.4896	1.4894	1.4903
4	1.4924	1.4907	1.4942	-----	1.4943	-----	1.4929	1.4945	1.4963	1.4960	1.4939
5	1.4924	1.4947	1.4955	-----	1.4934	-----	1.4942	1.4919	1.4922	1.4914	1.4932
6	1.4925	1.4909	1.4914	-----	1.4918	-----	1.4925	1.4906	1.4918	1.4952	1.4921
7	1.4971	1.4964	1.4979	-----	1.4969	-----	1.5001	1.4966	1.4956	1.4964	1.4971
8	1.4847	1.4856	1.4902	-----	1.4853	-----	1.4849	1.4842	1.4841	1.4839	1.4853
9	1.4964	1.4949	1.4961	-----	1.4945	-----	1.4956	1.4938	1.4945	1.4948	1.4951
10	1.4925	1.4931	1.4915	-----	1.4906	-----	1.4909	1.4892	1.4891	1.4900	1.4909
11	1.4941	1.4917	1.4935	1.4943	1.4926	1.4954	1.4920	1.4939	1.4922	1.4934	1.4934
Average apparent refractive index \bar{n}_a of one aromatic in several base stocks	1.4929	1.4920	1.4932	-----	1.4925	-----	1.4927	1.4923	1.4923	1.4928	1.4926
Value of n for pure aromatic	1.5001	1.4910	1.4963	1.4955	1.4954	1.4892	1.4898	1.4936	1.4927	1.4943	

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TABLE III - ANALYSIS OF BLENDS OF AROMATICS AND AROMATIC-FREE FUELS

n_x is the refractive index of blend
 n_b is the refractive index of base stock
 \bar{n}_a is the average apparent refractive index at 100-percent aromaticity

Fuel	Base stock	Aro- matic	n_x	n_b	\bar{n}_a	Aromaticity (percent by volume)		
						Prepared sample	Using \bar{n}_a	Using mean of \bar{n}_a (1.4926)
1	Esso Lab. No. 745-43	12	1.4134	1.3936	1.4937	20.0	19.8	20.0
		14	1.4034	1.3936	1.4937	10.0	9.8	9.9
		13	1.4060	1.3936	1.4937	12.5	12.4	12.5
		19	1.4136	1.3936	1.4937	20.0	20.0	20.2
		20	1.4283	1.3936	1.4937	35.0	34.7	35.1
2	Esso Lab. No. 744-43	12	1.4108	1.3965	1.4934	15.0	14.8	14.9
		14	1.4013	1.3965	1.4934	5.0	5.0	5.0
		20	1.4159	1.3965	1.4934	20.0	20.0	20.2
3	Texas-Hobbs crudes	14	1.4015	1.3915	1.4940	10.0	9.8	9.9
		19	1.3964	1.3915	1.4940	5.0	4.8	4.8
		21	1.4118	1.3915	1.4940	20.0	19.8	20.1
4	Sun Oil 91 octane	12	1.4139	1.4052	1.4921	10.0	10.0	10.0
		19	1.4357	1.4052	1.4921	35.0	35.1	34.9
		21	1.4229	1.4052	1.4921	20.0	20.4	20.2
5	Texas Co. 69 octane	20	1.4185	1.4053	1.4920	15.0	14.7	14.6
6	Texas Co. of Calif.	20	1.4067	1.4031	1.4925	3.8	4.0	4.0
7	Neohexane	12	1.3753	1.3689	1.4967	5.0	5.0	5.2
		19	1.3818	1.3689	1.4967	10.0	10.0	10.4
		21	1.3752	1.3689	1.4967	5.0	4.9	5.0
8	Cyclohexane	14	1.4305	1.4259	1.4885	7.5	7.3	6.9
		14	1.4381	1.4259	1.4885	20.0	19.5	18.3
11	S-2 refer- ence fuel	12	1.4116	1.3914	1.4940	20.0	19.7	20.0
		17	1.4116	1.3914	1.4940	20.0	19.7	20.0
		13	1.4018	1.3914	1.4940	10.0	10.1	10.3
Maximum error.							-0.5	-1.7
Mean deviation							±0.17	±0.22

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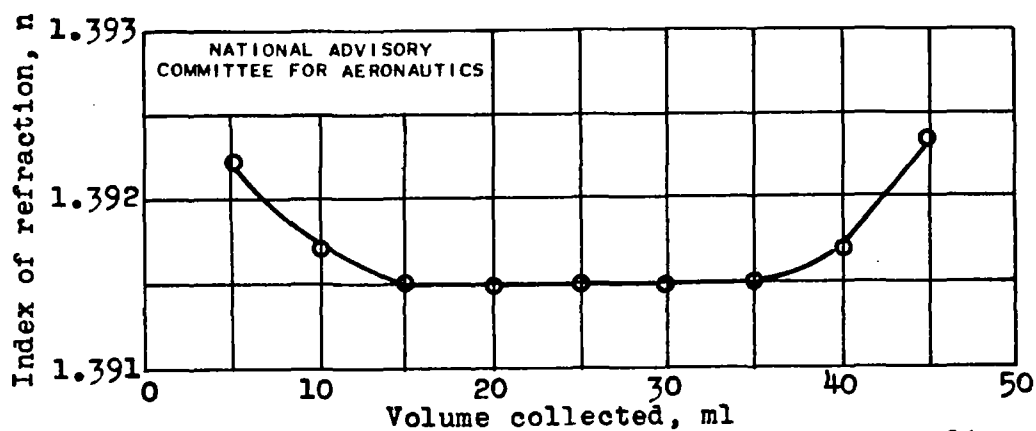


Figure 1. - Variation of index of refraction of gasoline sample upon removal of aromatics by percolation through silica gel. Composition, 20 percent benzene in Texas and Hobbs crude base stock; original index of refraction, 1.4117.

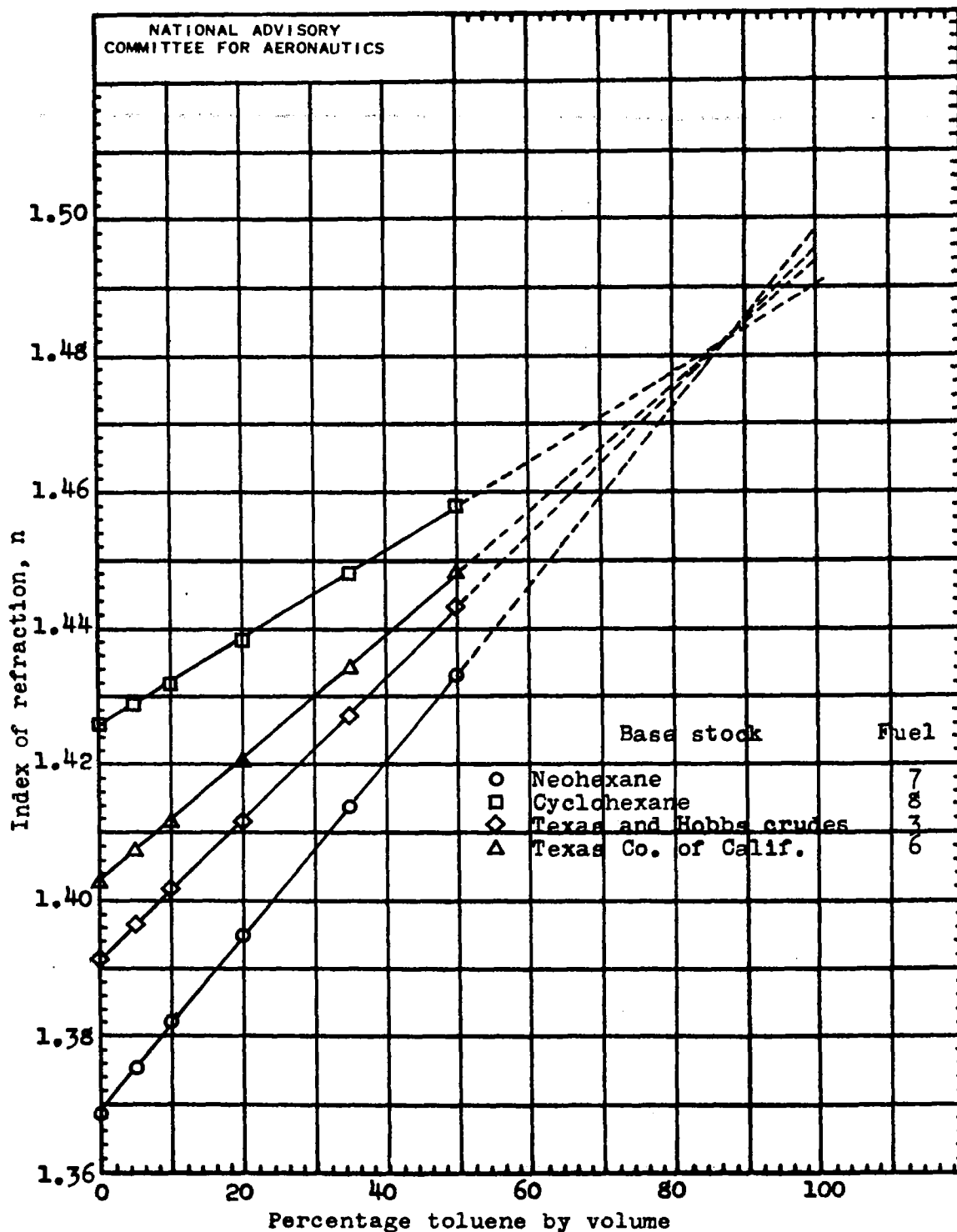


Figure 2. - Effect of toluene content of several gasoline base stocks upon index of refraction of the blends.

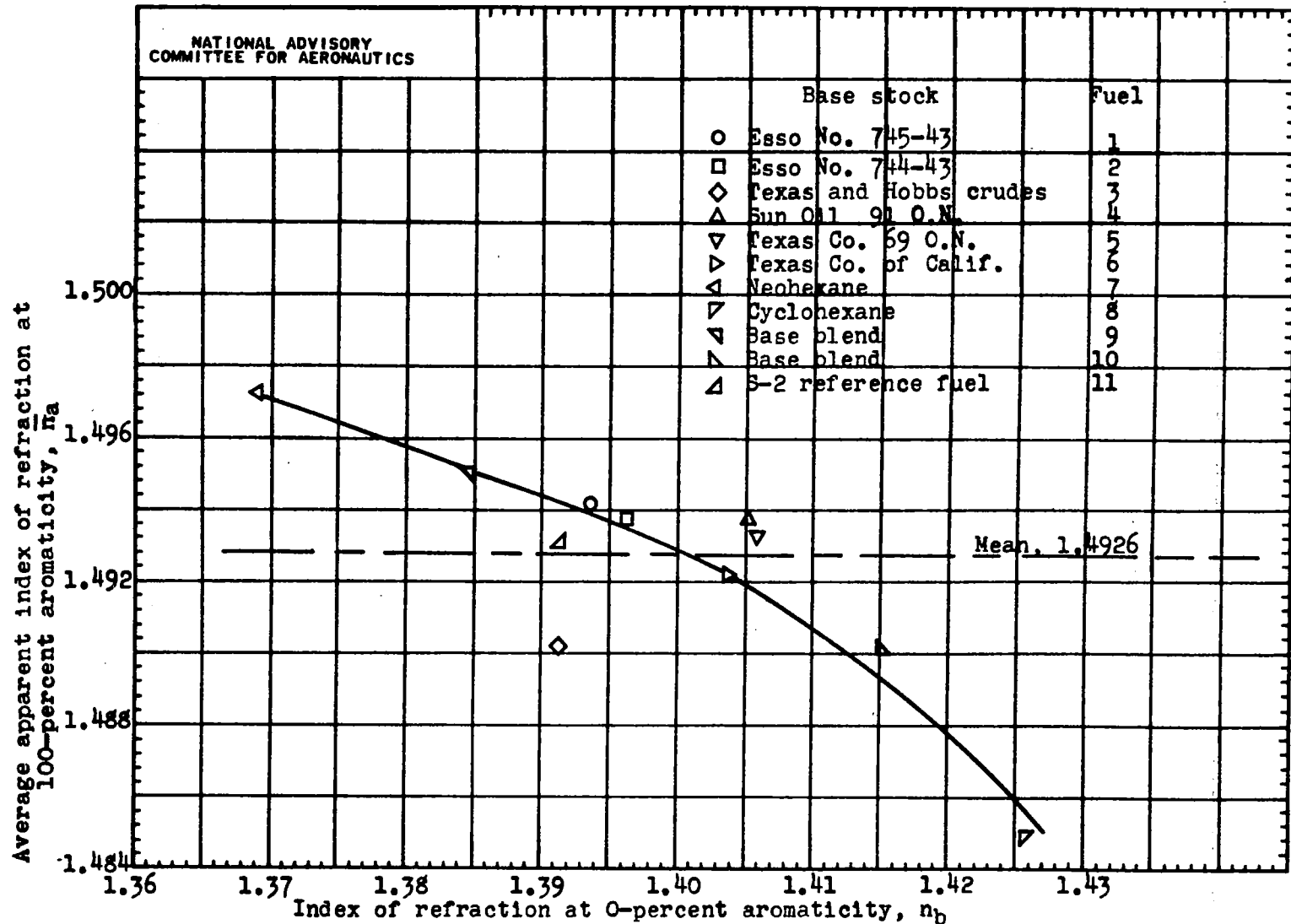


Figure 3. - Effect of gasoline base stock upon the average apparent index of refraction at 100-percent aromaticity for several aromatic blending agents.

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